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Microwave absorption and internal rotation in some dicyanoalkanes in benzene solution. part-I.

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In order to understand the dipole reorientation processes in flexible chain molecules, the dielectric permittivities and dielectric losses of three dicyanoalkanes in benzene solution have been measured at wave lengths 0.8, 1.25, 1.65 and 3.49 cm at different temperatures. The dielectric data could be represented by cole cole arc plots and were analysed in terms molecular reorientation and internal rotation of the $-CH_2$ CN groups. The potential barriers to molecular reorientation $\Delta H\tau_1$ and to internal rotation $\Delta H\tau_2$ have been determined. The temperature dependence of the apparent dipole moment was attributed to the presence of more than one conformer in each of the compounds. The increase in the distribution parameter α with increase in temperature in 1, 3 dicyanopropane has been explained.

1. INTRODUCTION

Studies on the dielectric absorption of microwaves in a number of alkylhalides (Higasi *et al* 1960, Vaughan *et al* 1962) showed that the results could be analysed in terms of relaxation times between two limits, the lower limit being determined by the segmental orientation of the terminal—CH_2 Br group and the upper limit corresponding to the end-over-end rotation of the entire molecule. Similar studies in the case of α,ω- dihaloalkanes (Garg *et al* 1973, Suresh Chandra *et al* 1972) with the two dipoles attached to the two terminals, showed that the results would be equally represented by Davidson-Cole skewed arc plots and also by the assumption of two independent Debye type absorption processes. In order to have a clear understanding of the dipole reorientation processes in flexible chain molecules, a programme was undertaken to extend similar studies in the case of a number dicyano-alkanes. In the present paper is reported the results obtained from the microwave absorption in 1, 2 dicyanoethane, 1, 3 dicyanopropane and 1, 4 dicyanobutane in benzene solution together with a discussion of the results.

2. Experimental

Chemicals: Pure samples of 1, 2 dicyanoethane, 1, 3 dicyanopropane and 1, 4 dicyanobutane were procured from Schuchardt (Germany). These were dried and distilled under reduced pressure before use in the investigations. The boiling points and refractive indices in all the liquids were in agreement with the literature values.

Apparatus: The apparatus for the measurement of dielectric permittivity ε' dielectric loss ε'' in the region 0.8, 1.25, 1.62 and 3.49 cm microwaves were described in an earlier paper (Das et al 1973). The static dielectric permittivity ε_0 was measured at 1 MHz, the refractive index n_D was determined with an Abbe refractometer The viscosity η and density d were measured with a Ostwald viscometer and a pycnometer respectively. The temperature in each experiment was kept constant within $\pm$ 1°C by means of a thermostat. The estimated errors in the determination of ε' and ε'' were about 2% and 4% respectively.

3. Results

The experimental values of ε' and ε'' at different microwave frequencies and at different temperatures are given in table 1. The values of ε_0, n^2_D, density (d) and viscosity η at different temperatures are given in table 2. Complex plane plots (figure 1) of the dielectric permittivity ε' and

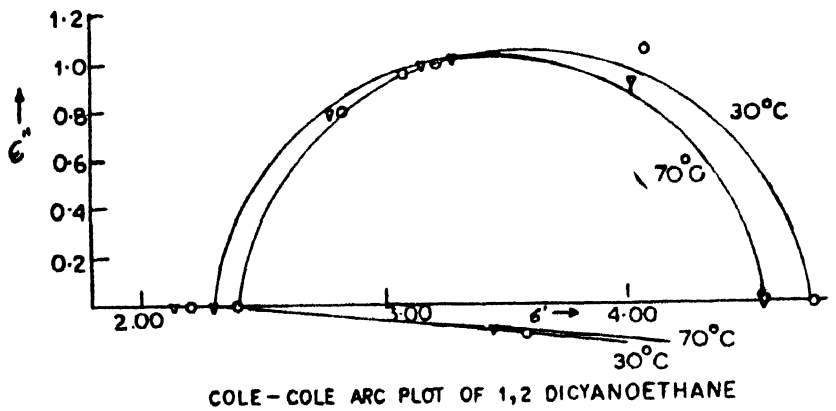
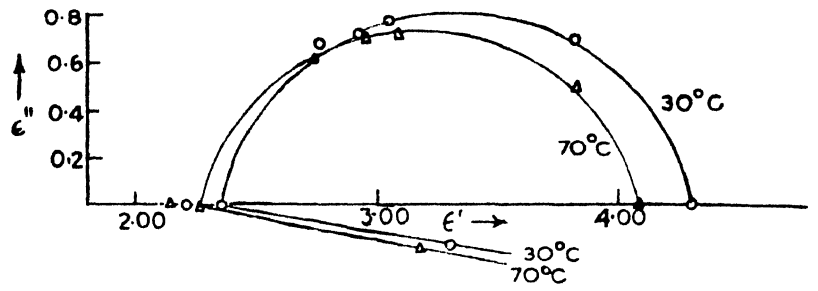
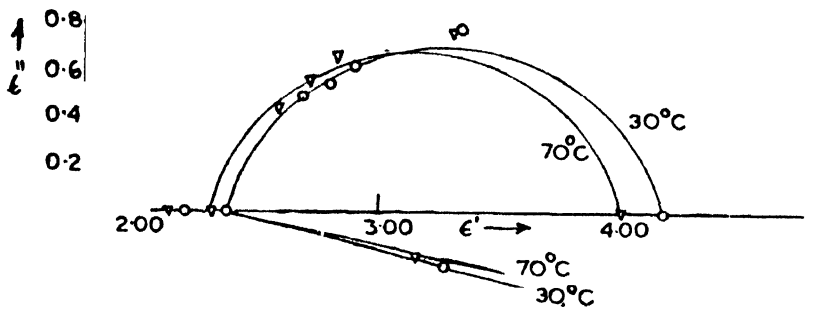


Fig 1

dielectric loss ε'' show a symmetric distribution with a depressed centre in each of the dicyanoalkanes at all temperatures, unlike the case in n alkylhalides (Vaughan *et al* 1962), α,ω- dihaloalkanes (Garg *et al* 1973, Suresh Chandra 1972) etc. where such plots showed assymmetric distribution. The distri-



COLE-COLE ARC PLOT OF 1,3 DICYANOPROPANE



COLE-COLE ARC PLOT OF 1,4 DICYANOBUTANE

Fig. 1

bution parameters α from the arc plots in the present dicyanoalkanes, were found appreciable at all temperatures, which is an indication of the presence of more than one relaxation processes in them. Attempts were then made to analyse the dielectric data in terms of two relaxation processes, making use of Bergmanns equations (1960)

$$a = \frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{c_1}{1+\omega^2\tau_1^2} + \frac{c_2}{1+\omega^2\tau_2^2} \qquad \ldots\ldots(1)$$

$$b = \frac{\varepsilon''}{\varepsilon_0 - \varepsilon_\infty} = \frac{c_1\omega\tau_1}{1+\omega^2\tau_1^2} + \frac{c_2\omega\tau_2}{1+\omega^2\tau_2^2} \qquad \ldots\ldots(2)$$

from which was derived a simplified linear equation.

$$Sx - Py - 1 = 0 \qquad \ldots\ldots(3)$$

where $S = \tau_1+\tau_2$, $P = \tau_1\tau_2$, $x = \dfrac{b\omega}{1-a}$ and $y = \dfrac{a\omega^2}{1-a}$

Table 1. Observed and calculated values of dielectric permittivities and dielectric losses in benzene solution. Concentrations are in mole fractions

t°C	f = 8.6 GHz				f = 24.05 GHz				f = 24.05 GHz				f = 36.2 GHz			
	ε'_{Obs}	ε'_{Cal}	ε''_{Obs}	ε''_{Cal}	ε'_{Obs}	ε'_{Cal}	ε''_{Obs}	ε''_{Cal}	ε'_{Obs}	ε'_{Cal}	ε''_{Obs}	ε''_{Cal}	ε'_{Obs}	ε'_{Cal}	ε''_{Obs}	ε''_{Cal}
.098 1, 2 dicyanoethane in benzene																
30	4.05	4.04	1.06	1.03	3.22	3.28	1.00	1.04	3.08	3.05	.96	95	2.82	2.78	.80	77
45	4.04	4.04	.98	.97	3.25	3.31	1.02	1.03	3.12	3.07	.98	96	2.81	2.80	.79	.79
60	4.02	4.02	.90	.89	3.28	3.33	1.00	1.01	3.15	3.09	98	95	2.78	2.80	79	81
.085 1, 3 dicyanopropane in benzene																
30	3.81	3.66	.70	.77	3.05	3.16	78	.80	2.92	2.98	.73	76	2.76	2.74	.68	66
45	3.80	3.65	.61	.72	3.08	3.16	76	76	2.94	3.00	72	72	2.75	2.77	.63	64
60	3.82	3.61	.50	.66	3.08	3.16	.72	.72	2.95	3.01	70	70	2.74	2.79	62	65
.073 1, 4 dicyasobutane in benzene																
30	3.34	3.34	.78	.76	2.91	2.92	.62	.61	2.75	2.75	52	.55	2.70	2.68	48	47
45	3.31	3.32	.76	.77	2.85	2.85	.60	.61	2.75	2.75	.52	.52	65	2.64	.42	.41
60	3.32	3.33	.76	.76	2.84	2.83	64	.64	2.73	2.72	.56	.55	2.60	2.60	.43	.42

The equation (3) was solved by the method of least squares described in an earlier paper (Roy *et al* 1976). The calculations for the determination of τ_1, τ_2, c_1 were carried out on IBM computer 1130. The calculated values ε', ε'' are included in table 1 for comparison with the observed values. The values of τ_1, τ_2, c_1 at different temperatures are given in table 3 and those of ε_∞ are included in table 2. The barriers to molecular reorientation

Table 2. Values of ε_0, n^2_D, ε_∞, d, η of the dicyanoalkanes in benzene solution.

t°C	ε_0	n^2_D	ε_∞	$d_{gm/cc}$	$\eta_{c.p.}$
		1, 2 dicyanoethanem benzene			
30	4.78	2.20	2.40	.878	47
45	4.68	2.18	2.36	.867	42
60	4.55	2.15	2.30	.850	.36
		1, 3 dicyanopropane in benzene			
30	4.30	2.21	2.35	.880	50
45	4.20	2.17	2.35	.865	.42
60	4.08	2.15	2.27	.850	36
		1, 4 dicyanobutane in benzene			
30	4.20	2.21	2.38	.874	50
45	4.10	2.19	2.38	.864	44
60	4.02	2.15	2.32	.850	38

$\Delta H\tau_1$ and to internal rotation $\Delta H\tau_2$ were obtained from the straight line plots of log log τ_1 T vs $\frac{1}{T}$ and log T τ_2 vs $\frac{1}{T}$ respectively. The heat of activation for viscous flow was obtained from the plot of log η vs $\frac{1}{T}$ The dipole moment μ was calculated from the equation (Tay and Crossley 1972)

$$\mu^2 = \frac{9kT\ (\varepsilon_0 - \varepsilon_\infty)\ (2\varepsilon_0 + \varepsilon_\infty)}{4\pi N \qquad \varepsilon_0(\varepsilon_\infty + 2)^2} \tag{4}$$

where N is the number of solute molecules per ml of the solution.

The values of $\Delta H\tau_1$, $\Delta H\tau_2$, $\Delta H\eta$ and μ are included in table 3.

4. Discussion

Molecular and internal relaxation time. It can be seen from table 3 that the larger relaxation times τ_1 at any temperature in 1, 2-, 1, 3- and 1, 4- dicyanoalkanes respectively are consistent with the increasing sizes of the molecules

and are evidently the molecular relaxation times. The molecular relaxation time τ_1 of 22.6 p.s at 30°C in 1, 4 dicyanobutane is comparable with the molecular relaxation time of 23 p sec. at 25°C in 1, 4 dibromobutane (Grag *et al* 1973).

Table 3. Values of α, τ_1, τ_2, C_1, $\Delta H\tau_1$, $\Delta H\tau_2$, $\Delta H\eta$ and μ in the dicyanoalkanes in benzene solution, conc in mole fraction

t°C	α	$\tau_1 \times 10^{12}$Sec	$\tau_2 \times 10^{12}$Sec	C_1	$\Delta H\tau_1$ kcal/mol	$\Delta H\tau_2$ kcal/mol	$\Delta H\eta$ kcal/mol	μ (Debye)
			098 1, 2 dicyanoethane					
30	070	14.3	4 8	80				3.50
45	065	13 1	4.1	80	0 64	1 20	2.09	3 57
60	060	11 8	3 6	79				3 65
			085 1, 3 dicyanopropane					
30	10	20 6	5 8	81				3 66
45	11	17 0	4 6	60	1 34	2 42	2 06	3 68
60	.13	15 8	3 7	57				3 79
			073 1, 4 dicyanobutane					
30	.16	22 6	3 6	79				3 86
45	14	19 8	2 3	84	1 24	3 69	2 02	3 88
60	.13	17.1	1 8	85				3.98

The shorter relaxation time τ_2 lying in the range 4-5.8 p s at 30°C, compare well with the relaxation time 6.5 p.sc. at 30°C of the acetonitril (CH_3CN) (Eloranta & Kadaba 1971) molecule in benzene solution and is most probably due to the rotation of the CH_2CN groups in each of the dicyanoalkanes. It may be noted that both the melecular and intramolecular relaxation times decrease with increase of temperature of the solutions as is usually observed in polar liquids.

Distribution parameter. The distribution parameter α (table 2) in 1, 2 – and 1, 4 – dicyanoalkane, decreases as usual with increase of temperature, but in the case of 1, 3 dicyanopropane, the α-value increases with increase in temperature. Similar increae in the value in 1, 3 prepane dithiol (Roy

et al 1976) at higher temperatures was attributed to the increase in the proportion of the higher energy TT conformer which, being more extended than the other conformers GG and TG, has got a larger relaxation time than the other two forms, so the same explanation is applicable for the increase in α–value at higher tmperature in the 1, 3 dicyanopropane which also has three conformers in the liquid state (Matsubara 1961, Yamadera 1958, Thorjornsrud 1972). Further it can be seen that at any temperature, the α–value is in the increasing order from 1, 2 dicyanoethane to 1, 4 dicyanobutane, probably due to the number of segmental oscillation around the various C-C bonds increase, with the increase in number of such bonds.

Weight factors. The molecular reorientation is found to be (table 2) the major relaxation process in 1, 2 - and 1, 4 - dicyanoalkanes, whereas in 1, 3 dicyanopropane the contribution from the internal roration ($C_2 \approx 45$) is only a little less than that of the molecular relaxation.

Barrier to molecular and internal rotation. The barrier to molecular reorientation ($\Delta H\tau_1$) in 1, 2 dicyanoethane and 1, 3 dicyanopropane in benzene solution are about 0.64 and 1.34 kcal/mol respectively and are about half the value of the barrier to internal rotation of (1.2 and 2.42 kcal/mol) the $-CH_2CN$ groups in the respective molecules. In the case of 1, 4 dicyanobutane the barrier to internal rotation ($\Delta H\tau_2 \approx 3.69$ kcal/mol) is about three times as large as that due to the molecular reorientation. It is also noted that the barrier to internal rotation increases with the increase in the number of C-C rotational axes.

Dipole momnt. In all the three dicyanoalkanes in benzene solution, the apparent dipole moment (table 3) is found to increase with increase of temperature of the solution indicating thereby the presence of more than one conformer in each of them and that the conformer with higher moment is of higher energy form. From spectroscopic studies it is reported that in 1, 2 dicyanoethane in the pure liquid state there exist two conformers trans and gauche, the latter being of the lower energy form but having higher dipole moment. In the present studies, in 1, 2 dicyanoethane in benzene solution, the conformer having higher dipole moment is of higher energy form, which is just opposite to that in pure liquid. The difference in behavier in pure liquid and in solution, may be explained as due to the molecular association in the pure liquid but in solution such association does not exist.

In the case of 1, 3 dicyanopropane (Thorjornsrud 1972) in the liquid state, three forms GG, TG and TT are present, the former two forms are in comparable proportion while the TT form present in minute proportion. From the bond moment and bond angle calculations, the dipole moment of GG

($\mu \approx 3.8D$) and TG ($\mu \approx 4.0D$) (Fig. 2) are nearly the same and that of TT form ($\mu \approx 4.5D$) is appreciably highr.

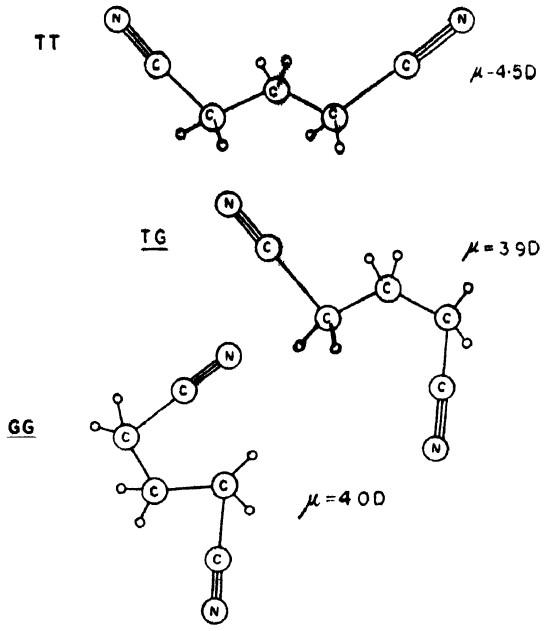


Fig. 2. Molecular configurations of 1, 3 dicyanopropanc.

So the increase in the apparent dipole moment with increase in temperature in this liquid may be attributed to the increase in the proportion of the TT form at higher temperature. This is also supported by the increase in the distribution parameter α at higher temperatures as mentioned earlier.

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